

Electronic Interactions in Organometallic Actinide Complexes

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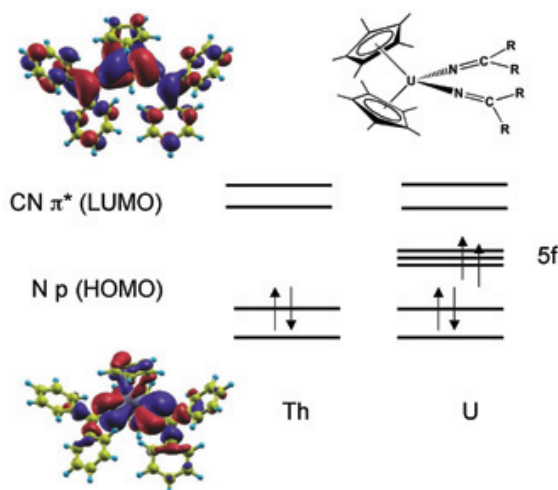
We have been examining the electronic interactions in organometallic complexes of the actinide and lanthanide elements using density functional theoretical (DFT) approaches. These interactions determine the chemical bonding in the ground state and define the nature of the excited electronic states as probed spectroscopic and magnetic techniques. One class of molecules synthesized and characterized extensively by our colleagues in the Chemistry Division are the ketimido complexes $(C_5R_5)_2M(N=CPh_2)_2$ where $M = Th$ and U and $R=CH_3$ (Ref. [1]). In each complex there is a metal in the +4 oxidation state, having either a $5f^0$ (Th) or $5f^2$ (U) electronic configuration, surrounded by two Cp^* (C_5R_5) and two nitrogen ketimido ligands. The optimized structures of the complexes as calculated using DFT agree well (typically within 0.01 – 0.02 Å) with values from experimental crystal structures. The results exhibit the expected shortening of the M-N bond length as one goes down the actinide

series from Th ($R = 2.25$ Å) to U ($R = 2.17$ Å). For the electronic excited states we have employed the time-dependent DFT method with the hybrid B3LYP functional to calculate the excited states of the system. As shown schematically in Fig. 1, the low-lying electronic states arise from excitations of the two highest occupied orbitals (HOMO), denoted lone pairs on the nitrogen (N 2p), to the two lowest unoccupied orbitals (LUMO), denoted pi antibonding (CN π^*). The theoretical assignments of excitations localized primarily on the ligand with some metal admixture is also borne out by the extensive experimental studies that have been carried out on Zr, Th and U ketimido complexes [2].

A major focus in this project has been the synthesis of assemblies comprised of two or more metal centers having unpaired f electrons and examining the resultant electronic coupling between the metal centers across the intervening organic linkages. Bimetallic ketimido analogs have been made containing two Th or U centers. Our results show the electronic structure mirrors the monometallic species with a similar set of orbitals involved in the excitations (except there are now four occupied and four virtual levels compared to Fig. 1). The calculated spectra for ketimido complexes with one and two Th centers are compared in Fig. 2, where the lowest observed energy absorption peak (~ 2.6 eV) arises from two singlet states (calc. 2.7 – 2.8 eV) in the monomeric species and from four singlet states (calc. 2.4 – 2.5 eV) in the dimeric species.

A second example of unusual bonding in organoactinide species is provided by another unusual bis-imido complex of uranium in the +6 oxidation state (Fig. 3). This represents the first known nitrogen complex with linear $(RN)=U=(NR)$ imido linkages analogous to the well-known uranyl $(O=U=O)^{2+}$ ion prevalent in solution chemistry

Fig. 1. Schematic diagram of the electronic structure of the $(C_5R_5)_2M(N=CPh_2)_2$ molecule showing the two highest occupied and two lowest unoccupied levels.



[3]. The NR groups can have either alkyl or phenyl substituents. Hybrid DFT calculations were used to understand the role of U 6d and 5f orbitals in the multiple bonds formed to the nitrogens and to compare with the bonding to oxygen in the uranyl species. The calculated U-N bond length (1.85 Å) and N-U-N bond angle (175 deg) for the complex shown in Fig. 3 (R=CH₃) are in close agreement with the experimental structures. We find strong admixture of 6d (up to 24%) and 5f (up to 32%) in the six molecular orbitals comprising the three U-N bonds that is also reminiscent of the metal participation in the uranyl ion. The vibrational frequencies were also computed to help in assignment of the infrared spectrum.

These illustrations demonstrate how current theoretical methods employing DFT can be applied to unravel issues in actinide chemistry using realistic ligands in the calculations.

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- [1] A.E. Clark, et al., *J. Phys. Chem. A* **109**, 5481 (2005).
- [2] R.E. Da Re, et al., *J. Am Chem. Soc.* **127**, 682 (2005).
- [3] T.W. Hayton, et al., *Science* **350**, 1941 (2005).

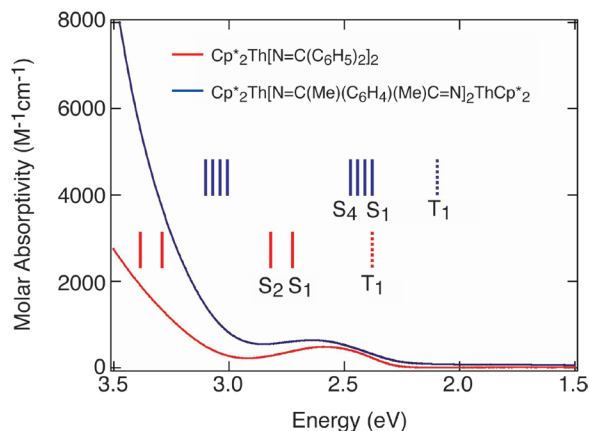


Fig. 2. Comparison of the predicted excitations for the mono- and bimetallic Th ketimido complexes from time-dependent DFT calculations with the observed experimental spectra. The excitations for these lowest states arise from the levels shown in Fig. 1.

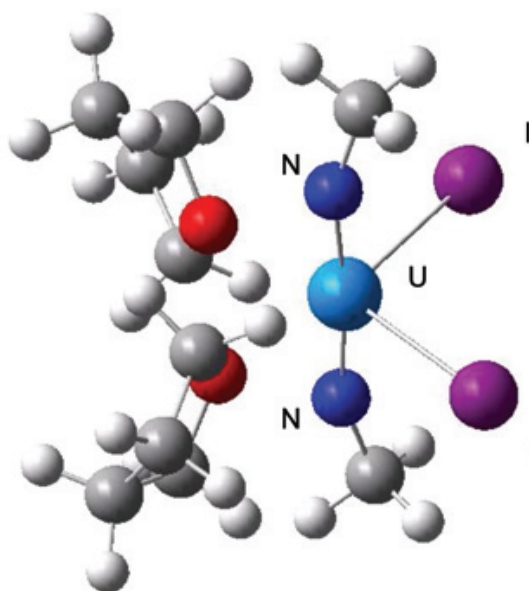


Fig. 3. Calculated structure of the U complex $U(=NCH_3)_2(I)_2(THF)_2$ that exhibits a linear $N=U=N$ bond as also observed in the crystal structures of several recently synthesized compounds. THF denotes tetrahydrofuran (C_4H_8O) ligand.